

Report of the Instrumental Techniques Committee, AOCS 1969-1970

Introduction

Following an established procedure, the Instrumental Techniques Committee met twice during the past year. The first meeting was held in conjunction with the 43rd Fall Meeting at the Leamington Hotel in Minneapolis, Minnesota, on October 6, 1969. The second meeting was held at the Jung Hotel in New Orleans, Louisiana, on April 27, 1970, during the 61st Annual Meeting.

Spectroscopy Subcommittee

A method permitting more rapid analysis of *trans* isomers in long chain fatty acids, esters or their triglycerides has been published in the *Journal* (1). The new simplified method, if found satisfactory, would afford a much more rapid analysis for isolated *trans* isomers in these commodities and would have the advantage of eliminating the need for external standards, a requirement of the present AOCS Method Cd 14-61. However, preliminary collaborative evaluation appeared to indicate that, while permitting a more rapid analysis, the new procedure is not as precise and is considerably limited in scope when compared to the present AOCS method. It cannot therefore be recommended as a revised method to replace Cd 14-61 (2). Following discussions of these early preliminary results, the Committee decided that the new rapid method had not been sufficiently tested and that further consideration should await its publication (2). During the past year, following the publication cited above (1), the Committee reconsidered the merits of the rapid procedure and decided that, although it probably could not be recommended as a replacement for Cd 14-61, it should be further investigated as an alternate procedure when highest precision is not required and when the specific analysis falls under the limited scope. The speed and simplicity of the new procedure could make it a very valuable alternate method, where applicable, to the present official method. It was agreed that the Spectroscopy Subcommittee should conduct further collaborative tests, including examination of fatty acids, esters and triglycerides containing constituents other than the mixtures of oleic and elaidic derivatives included in the preliminary collaborative tests. Specifically, mixtures containing stearates, linoleates, etc., should be investigated. The Subcommittee has embarked on this collaborative testing with the aim of recommending the new procedure as an alternate to Cd 14-61, where applicable.

Gas Chromatography Subcommittee

The Gas Chromatography Subcommittee has completed a detailed investigation to extend the scope of AOCS Official Method Ce 1-62 (Corrected 1964, Rev. 1968) particularly to include the use of flame detectors (2). A revised method has been accepted by the Instrumental Techniques Committee and referred to the Uniform Methods Committee with recommendation for its adoption as a further revision of Method Ce 1-62. Adoption of the newly revised method has been approved by the Uniform Methods Committee and the revised method will be included in the next edition of the Official Methods of the Society.

A request from the Codex Committee on Fats and Oils of the Joint Food and Agricultural Organization of the United Nations and World Health Organization, Codex Alimentarius Commission for specifications to define a specific vegetable oil or animal fat, based on its constituents as determined by gas chromatography, had been turned over to the Instrumental Techniques Committee for consideration by the Gas Chromatography Subcommittee. Subsequently specifications for 10 vegetable oils and animal

fats were furnished the Commission in time for their International Meeting in London, England, on September 16-20, 1968; (an 11th was added later). As interest in these specifications among members of the Society was rather high, they have been published in the *Journal* (3).

The Subcommittee has received several requests, suggestions and comments regarding the need for a gas chromatographic method for the determination of sterols in vegetable oils and animal fats, with the ultimate objective of including these data, along with the above-mentioned fatty acid data, as a more precise system for the identification of a specific oil or fat. The Subcommittee polled some 31 laboratories and found not only considerable interest but a relatively large number willing to participate in collaborative effort to establish specifications based on sterol constituents, as determined by gas chromatography (2). Consequently it was agreed that the Subcommittee should establish a Task Group to obtain the required data and to collaboratively evaluate its use for the identification of specific vegetable oils and animal fats.

Another problem which has been presented to the Subcommittee is the development of an analytical method, based on gas chromatography, for the detection and determination of pesticides in fats, oils and other lipid materials. In a pool simultaneously with the survey of interest in sterol determination, the Subcommittee established that there is not only considerable interest in this problem but again an appreciable percentage of the laboratories contacted were willing to participate actively in collaborative effort to establish a satisfactory procedure. Consequently the Committee agreed that such collaborative effort should be initiated by the Gas Chromatography Subcommittee. This collaborative effort may be conducted with cooperation of other interested Societies through the mechanism of the Intersociety Relations Committee.

X-Ray Diffraction Subcommittee

A high degree of inactivity among members of the X-Ray Diffraction Subcommittee prompted the Chairman to address a questionnaire to the 14 members asking for the following information:

1. Are you willing to continue to serve on the Subcommittee?
2. Can you suggest other members who might be interested in appointment to the Subcommittee?
3. Do you approve or disapprove the criteria of nomenclature for the monoacid saturated triglycerides in the report of the Subcommittee Chairman as published in the *Journal* (4)?
4. Will you volunteer to participate in further literature search?

Five members of the Subcommittee have not replied and two others submitted their resignations, reducing the Subcommittee to seven. Only three laboratories in this country are represented by this membership and five members, who are associated with these laboratories, have repeatedly mentioned their lack of time to devote to the necessary effort to pursue the objectives of the committee. No suggestions for new members were received. On results of acceptance or disapproval of the criteria of nomenclature for the monoacid saturated triglycerides, vote was almost equal for and against, these opposed suggesting further literature search, although no one would volunteer for such a search.

Based on the results of this questionnaire the Subcommittee Chairman reluctantly, but firmly, recommended to the Committee that "... in view of the limited interest in the application of x-ray diffraction to the field of fats and oils, this subcommittee be inactivated until further notice." This recommendation was, again reluctantly, ap-

¹ Report of collaborative work from Government, Industrial and Academic Laboratories by members of the ARS, USDA, Southern and Eastern Utilization Research and Development Divisions; Anderson, Clayton and Company, Food Division; The Hormel Institute, University of Minnesota; Durkee Fine Foods; and A. E. Staley Mfg. Co.

proved by the Committee and has been forwarded to the Uniform Methods Committee.

Subcommittee for the Preparation of Methyl Esters

The Subcommittee for the Preparation of Methyl Esters was created to devise a procedure whereby methyl esters could be prepared from either the free fatty acids or from triglycerides specifically for gas chromatography or infrared absorption analyses. For these purposes a technique was required which would not initiate any *cis-trans* or positional isomerization. The Subcommittee's work resulted in the adoption of AOCS Method Ce 2-66 based on a methanol-sulfuric acid esterification. Shortly after adoption of this procedure, however, literature reports appeared demonstrating much more rapid and much simpler procedures. As it became obvious that the slower AOCS official method would not be used, the Subcommittee inaugurated collaborative work to investigate the more rapid techniques. As a result of this effort AOCS method Ce 2-66 was revised, as recommended by the Subcommittee, and approved by the Committee by replacement with a more rapid and a simpler procedure using BF_3 -methanol. With this recommendation and Committee approval, the work of this Subcommittee was completed. However, suggestion that the Subcommittee be inactivated was held in abeyance pending approval of the revised method by the Uniform Methods Committee. During the past year Uniform Methods Committee approval was reached and consequently the Instrumental Techniques Committee approved the request that the Subcommittee be inactivated. This request for inactivation has been submitted to the Uniform Methods Committee.

Atomic Absorption Subcommittee

A first collaborative investigation of the determination of trace metals in oil was limited to the study of sodium and copper in corn oil. A collaborative study was made using two different analytical procedures. First, the samples were analyzed using the routine procedure in which weighed aliquots of oil were diluted with methyl isobutyl ketone and aspirated. Secondly, the analyses were repeated using the method-of-additions technique in which standards were added to suitable aliquots of the samples to reduce sample matrix effects. The purpose of this latter study was to determine if the method-of-additions technique would produce more accurate results than those of the routine technique. Results of these collaborative determinations are:

A. Synthetic sample: 4.50 ppm Na, 0.95 ppm Cu

Lab. No.	Sodium, ppm		Copper, ppm	
	Routine method	Additions method	Routine method	Additions method
1	3.96	4.30	1.24	0.87
2	4.80	5.70	0.91	0.73
3	5.38	6.30	1.15	1.05
4 (PE-290)	4.52	4.00	0.94	1.13
4 (PE-303)	4.47	4.06	1.33	1.73
5	3.90	5.20	0.90	1.00
6 ^a	1.50	1.50	0.60	0.72
7	5.23	4.15	1.14	1.04
Average	4.61	4.82	1.09	1.08
Standard deviation	0.585	0.981	0.227	0.345

^a Approximately three months elapsed before laboratory 6 was able to analyze the samples. Since the sodium values were too low to be explainable on the basis of experimental error, we concluded that the samples had deteriorated significantly prior to analysis. Therefore, none of the results from this laboratory was included in the statistical analysis.

B. Authentic sample: 0.156 ppm Na, 0.019 ppm Cu

Lab. No.	Sodium, ppm		Copper, ppm	
	Routine method	Additions method	Routine method	Additions method
1	0.21	0.06	0.15	0
2	0.12	0.17	0.1 ^a	ND
3	0.21	0.18	ND ^b	0.10
4 (PE-290)	0.06	0.01	0.12	0.13
4 (PE-303)	0.06	0.04	0.09	0.10
5	0	ND	0	ND
6	0.05	0.05	ND	ND
7	0.27	0.18	0.06	0.05
Average	0.133	0.09	0.07	0.05
Standard deviation	0.102	0.097	0.093	0.068

^a Value omitted from statistical analysis.

^b ND, not detected, treated as a zero value.

Synthetic Sample

Sodium Analyses. (a) The additions method did not yield greater accuracy and precision than the routine procedure. (b) The precision by both methods is rather poor. These conclusions were put on a quantitative basis by calculating 95% confidence limits for both methods. By the routine procedure these limits are 3.35 to 5.65 ppm, whereas for the additions procedure 2.57 to 6.43 ppm. Only 5% of the results would be expected to fall outside of these ranges, but these limits are still too wide to be acceptable.

Copper Analyses. Again confidence limits were established. For the routine method these limits are 0.41 to 1.39 ppm, and for the additions method 0.27 to 1.63 ppm. The conclusions drawn above are equally applicable to these results.

Authentic Sample

Sodium Analyses. The analysis of sodium by the routine procedure resulted in a range of values from 0 to 0.27 ppm with an average of 0.133 ppm. This average value, taking into consideration the low level of sodium actually present, is in good agreement with the 0.156 ppm sodium level in the authentic sample. However, the standard deviation for these results is 0.102 ppm indicating poor precision, which is readily apparent from the data tabulation. The 95% confidence limits for these results are -0.04 to 0.36 ppm.

Similar results for sodium were obtained by the additions procedure, although the average value was lower than in the above procedure (0.090 ppm compared to 0.133 ppm above). Again, the 95% confidence limits are rather wide, -0.03 ppm to 0.35 ppm.

Copper Analyses. Inasmuch as several collaborators were unable to detect the 0.019 ppm copper, the statistical data by either method are not too meaningful. These results do suggest, though, that at this low level, preconcentration procedures will have to be used before successful collaboration can be achieved.

From the 95% confidence limits of -0.16 to 0.20 ppm for the routine procedure and -0.11 to 0.15 ppm for the additions procedure, one could conclude with 95% assurance that the copper level is in fact below 0.2 ppm. However, future collaborative studies will be restricted to samples containing more copper than present in this authentic sample.

In summary this collaborative study indicated that the more convenient routine procedure should be used in future rounds of collaboration. Although the method-of-additions is often used to reduce sample matrix effects, the results of this study do not justify the additional time required to analyze oil samples by this technique. It seems likely that a direct method can be used for sodium and for other metals where their content is above the detection limit. Refined oils will probably require the use of a concentration step to isolate an enriched sample for metal analysis by atomic absorption.

The Subcommittee is now engaged in collaborative analyses for the direct measurement of metals in oils and fats, involving a precision study of the determination of iron, copper, sodium, nickel and chromium in soybean oil. To avoid difficulties where the trace metal content is close to the detection limits for the specific element, and acceptable precision is difficult to achieve without a prior concentration step, the concentrations of the metals have been adjusted to levels which should be conveniently measurable by all collaborators, using the routine procedure. Investigation of suitable concentration techniques is planned for later collaborative studies.

Wide-Line Nuclear Magnetic Resonance Subcommittee

By invitation, a group of members of the Society attended a meeting of the Instrumental Techniques Committee held during the 56th Annual Meeting in Houston, Texas, in 1965, to suggest the formation of a Subcommittee for the study of analytical techniques by means of Wide-Line Nuclear Magnetic Resonance Spectroscopy. During the following

Pilot Unit Determines Design Parameters of Steam-Jet Vacuum Equipment for Production Plants

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The efficient recovery of fatty acids and oils entrained in the deodorizing steam has the economic advantages of minimizing product loss and pollution in condenser water. To determine design and operating parameters for a full-scale production unit, a pilot unit was set up as a means of establishing flow rates, pressure, vacuum, temperature, load, type of mist eliminator and other factors that would operate most efficiently on a plant production scale.

The equipment in the pilot plant includes a 24 in. diameter Scrub-Vactor; a 12 sq ft, type 22-A ARM plate type heat exchanger; a 112 sq ft vapor-in-tube surface condenser with condensate tank; a 1¼ in. gear pump with steam turbine drive; a two-stage, noncondensing Evactor and a 200N Evactor vacuum pump.

The equipment was assembled as shown in the accompanying diagrams. The Scrub-Vactor is a combination of a jet-venturi fume scrubber and parallel flow condenser, which uses the product itself as the scrubbing medium.

Measured amounts of air, dry superheated steam and fatty acids is admitted to the Scrub-Vactor at a temperature of approximately 300 F, and a pressure of approximately 2 in. of Hg absolute. The inlet material is joined by a stream of distillate released at about 135 F and a pressure of 100 psig. The distillate is sprayed into the receiving area at just under atomization conditions. The inlet material and the distillate mixture is drawn into the venturi where they are thoroughly mixed and it is cooled to approximately 150 F. The distillate and the heavy oils which are condensed from the inlet mixture are returned to the charge at the bottom of the vessel. The charge is kept at a constant level by bleeding off the excess. The temperature is kept constant by circulation through the plate heat exchanger and returned to the high press spray nozzle.

The high temperature, high pressure distillate motivates

the flow and scrubs and condenses the vapor mixture being fed in. The purified water vapor remains in the vapor state because of the relatively high temperature, and passes upward through a mist eliminator and then into the surface condenser from which it is discharged. An extremely small amount of oil-laden vapor will pass through the scrubber in accordance with Dalton's Law of Additive Pressures.

Most runs of the pilot plant operation showed the efficiency resulted in a better than 95% recovery of the fatty acid oils. Samplings of the oils in the condensate showed a negligible contamination.

Weighted condensate samples were taken by inserting a tube into the condenser and drawing off a suitable amount of the fluid. Xylene was added to the sample to absorb any fatty oils that may have been present. The xylene and its absorbed oil (if any) floated to the surface and the sample was decanted leaving only the xylene mixture. Heat was then applied to drive off the xylene mixture. The amount of residual fatty oil remaining was formulated with the amount present in the inlet mixture and equated to a figure representing an efficiency percentage:

$$\text{Efficiency} = 1 - (\% \text{ oil residue} / \% \text{ oil inlet}) = 95\%$$

The residue figure was also checked by measuring the increase in distillate over a period of time and subtracting it from the amount of inlet oil.

During the test runs the heat transfer ratios for the plate cooler were worked out empirically for the various oils tested. These figures have proved valid when extrapolated for process equipment.

From the test logs and observations, apparent that production plant design and operating parameters were established and that the efficiency of the pilot tests could be simulated in full scale plant production.

Results also show that a Scrub-Vactor recovery unit can be placed in line in a continuous process equipment scheme without interrupting the functioning of the other chemical processing equipment as there is a minimal loss of pressure in this set-up.

Analysis and calculation of the test data results prove that the test data are practical as criteria for full scale equipment selection and operation. Also, use of the pilot unit assures an exceptionally high percentage of water-free product recovery and low contaminant condenser water.

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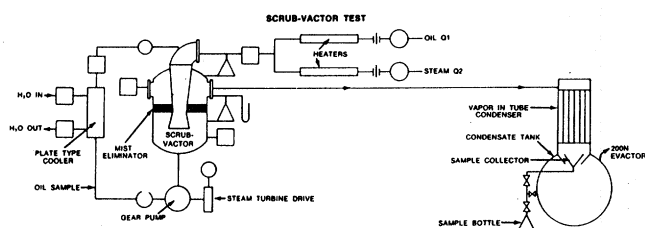


FIG. 1. Schematic drawing showing Croll-Reynolds Scrub Vactor test installation.

• Instrumental Techniques Committee . . .

(Continued from page 554A)

five-year period similar groups, arguing for the formation of such a Subcommittee, have appeared at almost all meetings of the Committee, mainly at the 1965 39th Fall Meeting in Cincinnati, at the 59th Annual Meeting in Washington in 1968, and at the San Francisco 60th National Meeting in 1969. These efforts have culminated during the past year in the formation of the Wide-Line Nuclear Magnetic Resonance Subcommittee of the Instrumental Techniques Committee. W. A. Bosin, The Pillsbury Company, 311 Second Street S.E., Minneapolis, Minn. 55414, has accepted appointment as Chairman of the new Subcommittee.

The Subcommittee is still in the process of formation. Among plans for early collaborative effort are the formation of Task Groups to investigate methods for determining

solid-fat indexes (SFI) by means of wide-line nuclear magnetic resonance spectroscopy, and collaborative study of methods for the determination of total oil content of vegetable oil samples also by wide-line nuclear magnetic resonance spectroscopy. Individual members interested in either of these activities are urged to contact Subcommittee Chairman William Bosin.

R. T. O'CONNOR, Chairman
R. R. ALLEN, Subcommittee Chairman
K. M. BROBST, Subcommittee Chairman
J. R. CHIPAULT, Subcommittee Chairman
S. F. HERB, Subcommittee Chairman
C. W. HOERR, Subcommittee Chairman

REFERENCES

1. Allen, R. R., JAOCS 46, 552 (1969).
2. O'Connor, R. T., R. R. Allen, K. M. Brobst, J. R. Chipault, S. S. Herb and C. W. Hoerr, JAOCS 46, 602A (1969).
3. O'Connor, R. T., and S. F. Herb, JAOCS 47, 186A (1970).
4. Hoerr, C. W., and F. R. Paulicka, JAOCS 45, 793 (1968).